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Polymer Science & Standards Division
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U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, *Secretary*

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SUMMARY

The objective of this work is the development of mathematical models that describe the migration of a variety of small molecules in polymers that have applications in food contact uses. In the most general cases, these models will be able to predict the amount of additive migration given any particular time and temperature history. These models can serve as the technical basis for more efficient regulatory methods under existing frameworks or in the design and implementation of new indirect additive regulations or policy.

The existing data on additive migration applicable to food contact uses have been surveyed and organized for reference. Existing models describing additive migration into food-simulating solvents have been surveyed and evaluated. From these considerations four main conclusions can be drawn:

1) At a given temperature above the glass transition of the polymer, diffusion in the polymer is invariably proportional to the concentration gradient of the diffusing species. The concentration gradient is the rate of change in concentration with distance in the polymer.

2) Diffusion in polymers below their glass transition is complex and difficult to generalize.

3) Above the glass transition temperature, the temperature dependence of diffusion is primarily determined by the properties of the polymer and relatively independent of the size and shape of the diffusant.

4) The temperature dependence of the diffusion is strong and non-Arrhenius. This means that a plot of the logarithum of the diffusion constant versus the inverse of the absolute temperature will generally be non-linear.

To model migration of minor constituents from a polymeric film to a food simulating solvent requires knowledge of (1) the equilibrium distribution of a migrant between polymer and solvent phases, i.e., the distribution or partition coefficient K and (2) the diffusion coefficient D of the migrant in the polymer. This is the minimum amount of information required to describe polymer/migrant/solvent system. For a polymer at a temperature above its glass transition temperature, knowledge of K and D allows one to calculate migration as a function of time and as a function of temperature if the temperature variation of K and D are also known.

We have shown that the distribution coefficient is related to the migrants' chemical potential in the polymer and solvent and have demonstrated how K and its temperature dependence can be calculated using recently developed theories of the chemical potential. Our preliminary calculations have been very encouraging. Additionally, K is amenable to experimental determination by utilization of gas chromatographic techniques.

Existing theories of the diffusion coefficient can be characterized as being correlative rather than predictive. We have formulated a new theory for D which promises to be more predictive than existing theories. This new theory is based on the thermodynamic theory of fluctuations and depends on: (1) the shape and size of the diffusant, (2) the polymer-diffusant intermolecular interactions, and (3) the isothermal compressibility of the polymer.

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INTRODUCTION

The effective regulation of indirect food additives arising from the migration of substances from plastic packaging materials involves three main technical questions:

1) What substances are present in the packaging material that can migrate into foods?

2) To what extent and at what rate can these substances be reasonably expected to migrate into the food?

3) What are the physiologic consequences of the ingestion of these quantities of these substances by the public?

The first of these questions can generally be answered by consideration of the synthesis and fabrication steps of the packaging material supported by straightforward analytical methods. The third question is a complex toxicological problem which at present can only be answered with case by case testing and even then is subject to considerable debate. The second question, however, is a measurement problem capable of general resolution and is the subject of this FDA-sponsored work.

The objective of this work is the development of mathematical models that describe the migration of a variety of small molecules in polymers that have applications in food contact uses. In the most general cases, these models will be able to predict the amount of additive migration given any particular time and temperature history. The models will be designed to require a minimum of laboratory data determined for the particular polymer-migrant system.

These models will serve several purposes. They can serve as a basis for the classification of polymers and additives into groups with similar migration behavior for regulatory purposes. They can reduce or eliminate the need for extensive extraction data to qualify new polymer-additive systems for food contact uses. For example, a change in a packaging process

requiring a higher filling temperature could be considered on the basis of an extrapolation from existing data without the need for additional laboratory work.

Physical models of migration can allow a relatively rapid estimate of maximum exposure of the public to any given additive or additive type. These estimates can guide public policy and provide a quantitative basis for toxicological assessments of risk. Finally, physical models or description of migration behavior can provide the technical information for a comprehensive review or adjustment of the total regulatory framework covering indirect food additives.

The first steps in the development and assessment of such models are given in this report. The first section presents a preliminary survey of migration data applicable to food contact situations that are available in the current literature. The second section surveys available models describing migration and evaluates their present and potential utility.

INTRODUCTION

The following literature survey collects and organizes available data on migration rates of low molecular weight species from polymeric matrices that have primary applicability to food contact situations. Only data that apply to food contact situations have been included. References that are useful in formulating and testing general models of migration will be added as the need arises. References prior to 1970 are also not explicitly included as these papers are adequately referenced in the cited, later work.

The ordered index is sorted first by type of polymer, then by the nature of the migrating species, and then by solvent. The abbreviations used are explained in the following section. The remarks primarily refer to the type of data presented and the time and temperature interval for which data are available.

KEY TO ABBREVIATIONS

******POLYMERS******

ABS	ACRYLONITRILE/BUTADIENE/STYRENE
ABS/MA	ABS/MA/MMA COPOLYMER
CA	CELLULOSE ACETATE
E/P	ETHYLENE/PROPYLENE
E/PHAC	ETHYLENE/PHENYL ACETATE
E/VAC	ETHYLENE/VINYL ACETATE
EPXR	EPOXY RESIN
FP	FLUOROPOLYMERS
MFR	MELAMINE FORMALDEHYDE RESIN
N6	NYLON 6
NR	NATURAL RUBBER
PA	POLYAMIDES
PAN	POLYACRYLONITRILE
PAT	POLYACETAL
PBD	POLYBUTADIENE
PDMS	POLYDIMETHYLSILOXANE
PE	POLYETHYLENE
PES	POLYESTER
PMA	POLYMETHACRYLATE
PMMA	POLY(METHYL METHACRYLATE)
PMP	POLY(4-METHYLPENTENE-1)
POM	POLYOXYMETHYLENE
PP	POLYPROPYLENE
PPHAC	POLYPHENYL ACETATE
PR	PHENOLIC RESIN
PS	POLYSTYRENE
PU	POLYURETHANE
PVC	POYL(VINLY CHLCRIDE)
PVC/ABS	POLY(VINYL CHLORIDE)/ABS
PVDC	POLY(VINYLIDENE CHLORIDE)
SAN	STYRENE/ACRYLONITRILE
SBR	STYRENE/BUTADIENE RUBBER
SR	SILICONE RUBBER
V/APB	VINYL ACETATE/VINYL PYRROLIDONE/VINYL BUTYL ETHER

******MIGRANTS******

ABC	ACETYL TRIBUTYL CITRATE
ACA	AMINOCROTONIC ACID ESTERS
AHA	1-AMINO-4-HYDROXYANTHRAQUINONE
AN	ACRYLONITRILE
BDO	BUTADIENE OLIGOMER
BHA	TERT-BUTYL-4-HYDROXYANISOLE

BHT	2,6-DI-TERT-BUTYL-P-CRESOL; IONOL; ADVASTAB 401
BPBG	BUTYL PHTHALYL BUTYLGLYCOLATE
BPD	BENZOPHENONE DERIVATIVES; DASTIB-244,-256,-280
BST	BUTYL STEARATE
BTA	BENZOTRIAZOLE-PHENOLS; TINUVIN P; TINUVIN 320
BTAC	CHLOROBENZOTRIAZOLE-PHENOLS; TINUVIN 326; TINUVIN 327
CAST	CALCIUM STEARATE
CD	CADMIUM PIGMENTS
DBP	DIBUTYL PHTHALATE
DBS	DIBUTYL SEBACATE
DBSN	DIBUTYL TIN COMPOUNDS
DCDA	DICYANDIAMIDE
DHA	1,4-DIHYDROXYANTHRAQUINONE
DHBP	2,4-DIHYDROXYBENZOPHENONE
DNP	DINONYL PHTHALATE
DOP	DIOCTYL PHTHALATE
DOSN	DIOCTYL TIN COMPOUNDS
DTCT	N-DOTRIACOTANE
DTP	DIDODECYL-3,3'-THIOPROPIONATE
HCHO	FORMALDEHYDE
HEBP	2-HYDROXY-4-(2'-ETHYLHEXYL)-OXYBENZOPHENONE; DASTIB 242
HMBP	2-HYDROXY-4-METHOXYBENZOPHENONE; UV ABSORBER MOB; ADVASTAB 45
HOBP	2-HYDROXY-4-OCTOXYBENZOPHENONE; ADVASTAB 46; CYASORB UV531
HXD	N-HEXADECANE
MGST	MAGNESIUM STEARATE
MMA	METHYL METHACRYLATE
MMBP	2,2'-METHYLENE-BIS-(4-METHYL-6-TERT-BUTYLPHENOL); 2246
MSN	METHYL TIN COMPOUNDS
MW	MICROWAX
NAAB	4-NITRO-4'-AMINOAZOBENZENE
ODE	N-OCTADECYL-DIETHANOLAMINE
OHBP	N-OCTADECYL-B-(4'-HYDROXY-3,5'-DI-T-BUTYLPHENYL)PROPIONATE
PAP	POLYADIPATE
PB	LEAD
PH	PHENOL
RP	ALKYL PHTHALATES
RSE	ALKYL SULFONIC ACID ESTERS
S	STYRENE
SA	STEARIC ACID AMIDE
SN	TIN COMPOUNDS
STP	DISTEARYL THIODIPROPIONATE; ADVASTAB PS802; ANTIOXYDANS AS
TBC	4,4'-THIO-BIS-(6-T-BUTYL-M-CRESOL); ADVASTAB 415; SANTONOX
TCP	TRICRESOL PHOSPHATE
TEP	TRIETHYL PHOSPHATE
TG	TRIGLYCERIDES
TIO2	TITANIUM DIOXIDE
TNPP	TRIS-(NONYLPHENYL) PHOSPHATE; ADVASTAB TNPP
TTB	1,3,5-TRIMETHYL-2,4,6-TRIS(3,5-DI-T-BUTYL-4-HYDROXYBENZYL)
VAC	VINYL ACETATE
VC	VINYL CHLORIDE
WAX	PARAFFIN WAX
XYZ	BENZENE; CHLOROBENZENE; ETHYLENE GLYCOL; ETHYL EHTER; ETHANOL; N-ALKANE
ZNST	ZINC STEARATE

******SOLVENTS******

AQ	AQUEOUS SOLUTIONS OF SALTS; DETERGENTS; ETC.
BL	BLOOD
DP	DAIRY PRODUCTS
ETOH	ETHANOL
ET2O	DIETHYL ETHER
FHC	FLUOROHYDROCARBON
HC	HYDROCARBONS
H2O	WATER
HOAC	ACETIC ACID
MEOH	METHANOL
MF	MEAT AND FAT
NH	N-HEPTANE
OIL	OIL; FAT AND SIMULANT
ROH	ALCOHOLS
R2O	ETHERS
TG	INDIVIDUAL TRIGLYCERIDES
VEG	VEGETABLE

******METHODS******

CA	CHEMICAL ANALYSIS
COLOR	COLORIMETRY
GC	GAS CHROMATOGRAPHY
GM	GRAVIMETRY
PHOTO	PHOTOMETRY
POLAR	POLAROGRAPHY
RAD	RADICANALYSIS
SECT	SECTIONAL ANALYSIS
SPEC	SPECTROSCOPY
TLC	THIN LAYER CHROMATORGRAPHY

******REMARKS******

AC	ACTIVITY COEFFICIENT
APP	APPARATUS/METHOD
CMT	CORRELATION/MODEL/THEORY
CP	CONCENTRATION GRADIENT PROFILE
D	DIFFUSION COEFFICIENT
ENI	EXTRACT NOT IDENTIFIED
GR	GRAPHS
H*	ACTIVATION ENERGY
K	PARTITION COEFFICIENT
MC	MIGRANT CONCENTRATION
NC	NO COMPOSITION
NKD	NO KINETIC DATA
NS	NO SURFACE AREA INFORMATION
NTT	NO TEMPERATURE OR TIME INFORMATION

PHR	PARTS PER HUNDRED PARTS OF RESIN
RT	ROOM TEMPERATURE
SD	SORPTION-DESORPTION
SECT	SECTIONAL OBSERVATION
SOL	SOLUBILITY
UNITS	C-CELCIUS; D-DAY; H-HOUR; M-MONTH; W-WEEK; Y-YEAR

ORDERED INDEX TO AVAILABLE DATA

POLYMER	MIGRANT	SOLVENT	METHOD	REMARKS (DATA POINTS AT TEMPERATURE/TIME)	REFERENCE
ABS	ABC	ETOH		NKD, TO 80C/TO 5D	124
ABS	ABC	H2O		NKD. TO 80C/TO 5D	124
ABS	AN	AQ		GR: RT/ TO 200D	144
ABS	AN	H2O		GR: RT/ TO 200D	144
ABS	BST	ETOH		NKD. TO 80C/TO 5D	124
ABS	BST	H2O		NKD. TO 80C/TO 5D	124
ABS	S	AQ		GR: RT/ TO 200D	144
ABS	S	ETOH		NKD. TO 80C/TO 5D	124
ABS	S	H2O		NKD. TO 80C/TO 5D	124
ABS	S	H2O		GR: RT/ TO 200D	144
ABS	XYZ			INTER-POLYMER. APP. 70C/TO 1320D	112
CA	DOP	ET2O	GC	NKD. TO 98C/TO 10D	10
CA	DOP	HC	GC	NKD. TO 98C/TO 10D	10
CA	DOP	OIL	GC	NKD. TO 98C/TO 10D	10
CA	DOP	TG	GC	NKD. TO 98C/TO 10D	10
CA	XYZ				100
E/P	HXD			D	141
EPXR				CMT	99
FP	HCHO	H2O		NKD. 0-90C/1-10D	122
MFR	HCHO	H2O		NKD	32
NR	DTCT			D	141
NR	WAX			TO 280D	19
NR	XYZ		GM	BLOOM	158
NR	XYZ			D. CMT. SMEAR	140
PA	CD	ETOH		80C/6H	190
PA	CD	ET2O		80C/6H	190
PA	CD	H2O		80C/6H	190
PA	CD	HOAC		80C/6H	190
PBD	HXD			D. CMT	139
PBD	HXD			D. CMT. SMEAR	140
PBD	HXD			D	141
PDMS	DTCT			D	141
PE	EHA	ET2O	GC	NKD. TO 98C/TO 10D	10
PE	EHA	HC	GC	NKD. TO 98C/TO 10D	10
PE	EHA	OIL	GC	NKD. TO 98C/TO 10D	10
PE	EHA	TG	GC	NKD. TO 98C/TO 10D	10
PE	BPD	ETOH		45C/2.10D. 70C/2H. 100.121C/0.5H	168
PE	BPD	H2O		45C/2.10D. 70C/2H. 100.121C/0.5H	168
PE	BPD	HOAC		45C/2.10D. 70C/2H. 100.121C/0.5H	168
PE	BPD	OIL		45C/2.10D. 70C/2H. 100.121C/0.5H	168
PE	ETAC	ETOH	TLC	NKD. 45C/10D	170
PE	ETAC	HC	TLC	NKD. 45C/10D	170
PE	ETAC	HC		GR: 40-65C/TO 60D	118
PE	ETAC	H2O	TLC	NKD. 45C/10D	170

PE	BTAC	HOAC	TLC	NKD, 45C/10D	170
PE	BTAC	OIL	POLAR	4,20-25C/1,2,3,6M, 45C/10D,6M	166
PE	BTAC	OIL	TLC	NKD, 45C/10D	170
PE	BTAC	OIL		GR: 40-65C/TO 60D	118
PE	CD	ETOH		80C/6H	190
PE	CD	ET2O		80C/6H	190
PE	CD	H2O		80C/6H	190
PE	CD	HOAC		80C/6H	190
PE	DHBP	H2C	RAD	CMT, D, 44-75C/TO 1000H	177
PE	DCP			INTER-POLYMER, APP, 70C/TO 1320D	112
PE	DTP		RAD	D, H*, CMT, SMEAR, 20-78C	73
PE	HEBP	ETOH		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HEBP	H2O		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HEBP	HOAC		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HEBP	OIL		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HMBP	ETOH	TLC	NKD, 45C/10D	170
PE	HMBP	HC	TLC	NKD, 45C/10D	170
PE	HMBP	H2O	TLC	NKD, 45C/10D	170
PE	HMBP	HOAC	TLC	NKD, 45C/10D	170
PE	HMBP	OIL	TLC	NKD, 45C/10D	170
PE	HOBP	ETOH		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HOBP	H2O	RAD	D, H*, SMEAR, EXTRACT @44C/TO 255D	77
PE	HOBP	H2O		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HOBP	HOAC		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	HOBP	OIL		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PE	MMBP		RAD	D, K, INTER-POLYMER	13
PE	ODE		RAD	D, H*, CMT, SMEAR, 20-78C	73
PE	SA	ET2O	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	SA	FHC	RAD	20C/43,60D	54
PE	SA	HC	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PE	SA	HC	RAD	20C/43,60D	54
PE	SA	HC	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	SA	MEOH	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	SA	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PE	SA	OIL	RAD	20C/30,60D	45
PE	SA	OIL	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PE	SA	OIL	RAD	65C/2.5H, GR: TO 6H	51
PE	SA	OIL	RAD	20C/30,60D, GR: TO 60D	52
PE	SA	OIL	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2.5H	53
PE	SA	OIL	RAD	20C/43,60D	54
PE	SA	OIL	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	SA	R2C	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PE	SA	R2O	RAD	20C/43,60D	54
PE	SA	TG	RAD	65,83C/2.5H	38
PE	SA	TG	RAD	20C/30,60D	45
PE	SA	TG	RAD	65C/2.5H, GR: TO 6H	51
PE	SA	TG	RAD	20C/30,60D, GR: TO 60D	52
PE	SA	TG	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2.5H	53
PE	SA			SURFACE	50
PE	TTB	ET2O	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	TTB	FHC	RAD	20C/43,60D	54
PE	TTB	HC	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PE	TTB	HC	RAD	20C/43,60D	54
PE	TTB	HC	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	TTB	MEOH	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	TTB	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PE	TTB	OIL	RAD	20C/30,60D	45
PE	TTB	OIL	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46

PE	TTB	OIL	RAD	65C/2.5H, GR: TO 6H	51
PE	TTB	OIL	RAD	20C/30,60D, GR: TO 60D	52
PE	TTB	OIL	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2.5H	53
PE	TTB	OIL	RAD	20C/43,60D	54
PE	TTB	OIL	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PE	TTB	R2O	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PE	TTB	R2O	RAD	20C/43,60D	54
PE	TTB	TG	RAD	65,83C/2.5H	38
PE	TTB	TG	RAD	20C/30,60D	45
PE	TTB	TG	RAD	65C/2.5H, GR: TO 6H	51
PE	TTB	TG	RAD	20C/30,60D, GR: TO 60D	52
PE	TTB	TG	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2.5H	53
PE	XYZ	H2O		TO 50C/TO 8W	119
PE					66
PE			RAD	D, H*, CMT, SMEAR, 20-78C	73
PE		OIL		FAT-MIGRATION	96
PMA	DBP	ETOH	POLAR	NKD, 45C/10D	189
PMA	DBP	HC	POLAR	NKD, 45C/10D	189
PMA	DBP	H2O	POLAR	NKD, 45C/10D	189
PMA	DBP	HOAC	POLAR	NKD, 45C/10D	189
PMA	DOP	ETOH	POLAR	NKD, 45C/10D	189
PMA	DOP	HC	POLAR	NKD, 45C/10D	189
PMA	DOP	H2O	POLAR	NKD, 45C/10D	189
PMA	DOP	HOAC	POLAR	NKD, 45C/10D	189
PMMA	HMBP	ETOH	TLC	NKD, 45C/10D	170
PMMA	HMBP	HC	TLC	NKD, 45C/10D	170
PMMA	HMBP	H2O	TLC	NKD, 45C/10D	170
PMMA	HMBP	HOAC	TLC	NKD, 45C/10D	170
PMMA	HMBP	OIL	TLC	NKD, 45C/10D	170
PMMA	MMA	H2O		CMT, GR: 37-90C/10H	162
PMMA	XYZ				109
PMP	DTP		RAD	D, H*, CMT, SMEAR, 20-78C	73
PMP			RAD	D, H*, CMT, SMEAR, 20-78C	73
POM	DCDA	H2O	PHOTO	37C/1,3,5,7D, 100C/2H, GR: TO 10D	97
POM	HCHO	H2O	PHOTO	37C/1,3,5,7D, 100C/2H, GR: TO 10D	97
POM	MMBP	H2O	PHOTO	37C/1,3,5,7D, 100C/2H, GR: TO 10D	97
PP	BHT			NKD, 45C/10D	167
PP	ETAC	HC		GR: 40-65C/TO 60D	118
PP	ETAC	OIL		GR: 40-65C/TO 60D	118
PP	OHBP	H2O	RAD	CMT, D, 44-75C/TO 1000H	177
PP	DTP		RAD	D, H*, CMT, SMEAR, 20-78C	73
PP	HOBP	ETOH		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PP	HOBP	H2O		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PP	HOBP	HOAC		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PP	HOBP	OIL		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PP	ODE		RAD	D, H*, CMT, SMEAR, 20-78C	73
PP	OHBP	HC		GR: 40-65C/TO 60D	118
PP	OHBP	OIL		GR: 40-65C/TO 60D	118
PP			RAD	D, H*, CMT, SMEAR, 20-78C	73
PR	HCHO			NC, 20-80C	165
PR	PH			NC, 20-80C	165
PS	BHT	ET2O	GC	NKD, TO 98C/TO 10D	10
PS	BHT	HC	GC	NKD, TO 98C/TO 10D	10
PS	BHT	OIL	GC	NKD, TO 98C/TO 10D	10
PS	BHT	TG	GC	NKD, TO 98C/TO 10D	10
PS	BHT			NKD, 45C/10D	167
PS	BST	ET2O	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	BST	FHC	RAD	20C/43,60D	54

PS	BST	HC	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	BST	HC	RAD	20C/43,60D	54
PS	BST	HC	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	BST	H2C		GR: 60C/TO 1Y	128
PS	BST	MECH	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	BST	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PS	BST	OIL	RAD	20C/30,60D	45
PS	BST	OIL	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	BST	OIL	RAD	65C/2,5H, GR: TO 6H	51
PS	BST	OIL	RAD	20C/30,60D, GR: TO 60D	52
PS	BST	OIL	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PS	BST	OIL	RAD	20C/43,60D	54
PS	BST	OIL	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	BST	R2O	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	BST	R2C	RAD	20C/43,60D	54
PS	BST	TG	RAD	65,83C/2,5H	38
PS	BST	TG	RAD	20C/30,60D	45
PS	BST	TG	RAD	65C/2,5H, GR: TO 6H	51
PS	BST	TG	RAD	20C/30,60D, GR: TO 60D	52
PS	BST	TG	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PS	BST			CMT, D, 20,40,60C/100D, GR: 10-100D	174
PS	CD	ETOH		80C/6H	190
PS	CD	ET2O		80C/6H	190
PS	CD	H2C		80C/6H	190
PS	CD	HOAC		80C/6H	190
PS	DOP	ETOH		NKD, TO 80C/TO 5D	124
PS	DOP	H2C		NKD, TO 80C/TO 5D	124
PS	HMBP	ETOH	TLC	NKD, 45C/10D	170
PS	HMBP	HC	TLC	NKD, 45C/10D	170
PS	HMBP	H2C	TLC	NKD, 45C/10D	170
PS	HMBP	HOAC	TLC	NKD, 45C/10D	170
PS	HMBP	OIL	TLC	NKD, 45C/10D	170
PS	HOBP	ETOH		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PS	HOBP	H2C		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PS	HOBP	HOAC		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PS	HOBP	OIL		45C/2,10D, 70C/2H, 100,121C/0.5H	168
PS	HXD			D, CMT, SMEAR	140
PS	PAP			INTER-POLYMER, APP, 70C/TO 1320D	112
PS	S	AQ		NTT, 1,3,5D	126
PS	S	DP	GC	CMT, D, GR: TO 20C/TO 30D	29
PS	S	ETOH		GR: 23-70C/0.01-720D	131
PS	S	H2C	GC	CMT, D, GR: TO 20C/TO 30D	29
PS	S	H2C		NTT, 1,3,5D	126
PS	S	H2C		GR: 60C/TO 1Y	128
PS	S	H2C		GR: 23-70C/0.01-720D	131
PS	S	H2C		CMT, GR: 37-90C/10H	162
PS	S	HOAC		NTT, 1,3,5D	126
PS	S	HOAC		GR: 23-70C/0.01-720D	131
PS	S	OIL		NTT, 1,3,5D	126
PS	S	OIL		GR: 23-70C/0.01-720D	131
PS	S			CMT, D, 20,40,60C/100D, GR: 10-100D	174
PS	STP			NKD, 45C/10D	167
PS	TBC			NKD, 45C/10D	167
PS	TNPP			NKD, 45C/10D	167
PS	TTB	ET2O	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	TTB	FHC	RAD	20C/43,60D	54
PS	TTB	HC	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	TTB	HC	RAD	20C/43,60D	54

PS	TTB	HC	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	TTB	MECH	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	TTB	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PS	TTB	OIL	RAD	20C/30,60D	45
PS	TTB	OIL	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	TTB	OIL	RAD	65C/2,5H, GR: TO 6H	51
PS	TTB	OIL	RAD	20C/30,60D, GR: TO 60D	52
PS	TTB	OIL	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PS	TTB	OIL	RAD	20C/43,60D	54
PS	TTB	OIL	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PS	TTB	H2O	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PS	TTB	R2O	RAD	20C/43,60D	54
PS	TTB	TG	RAD	65,83C/2,5H	38
PS	TTB	TG	RAD	20C/30,60D	45
PS	TTB	TG	RAD	65C/2,5H, GR: TO 6H	51
PS	TTB	TG	RAD	20C/30,60D, GR: TO 60D	52
PS	TTB	TG	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PS	XYZ	H2O		TO 50C/TO 8W	119
PS	XYZ				100
PS	XYZ			CMT, SD	172
PU	DHBP		RAD	D, H*, SMEAR, 36-75C/TO 30D	69
PU	HOBP		RAD	C, H*, SMEAR, 36-75C/TO 30D	69
PVC	ABC	ET2O	GC	NKD, TO 98C/TO 10D	10
PVC	ABC	HC	GC	NKD, TO 98C/TO 10D	10
PVC	ABC	OIL	GC	NKD, TO 98C/TO 10D	10
PVC	ABC	TG	GC	NKD, TO 98C/TO 10D	10
PVC	ABC			20C/1,3,7D	83
PVC	ACA	OIL		4,20-25C/1,2,3,6M, 45C/10D	167
PVC	BPBG			20C/1,3,7D	83
PVC	ETA	ETOH	TLC	NKD, 45C/10D	170
PVC	ETA	HC	TLC	NKD, 45C/10D	170
PVC	ETA	HC		GR: 40-65C/TO 60D	118
PVC	ETA	H2O	TLC	NKD, 45C/10D	170
PVC	ETA	HOAC	TLC	NKD, 45C/10D	170
PVC	ETA	OIL	POLAR	4,20-25C/1,2,3,6M, 45C/10D,6M	166
PVC	ETA	OIL	TLC	NKD, 45C/10D	170
PVC	ETA	OIL		GR: 40-65C/TO 60D	118
PVC	CAST	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	DBP	ETOH	RAD	25C/TO 50D	79
PVC	DBP	ETOH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DBP	ET2O	GC	NKD, TO 98C/TO 10D	10
PVC	DBP	HC	GC	NKD, TO 98C/TO 10D	10
PVC	DBP	HC	RAD	20-60PHR, 10-60C/2-80D	79
PVC	DBP	MEOH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DBP	OIL	GC	NKD, TO 98C/TO 10D	10
PVC	DBP	OIL	RAD	20-60PHR, 10-60C/1-70D	81
PVC	DBP	ROH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DBP	TG	GC	NKD, TO 98C/TO 10D	10
PVC	DBP		RAD	20-60PHR, 10-60C/1-70D	81
PVC	DBS			20C/1,3,7D	83
PVC	DBSN	AQ		50C/2,4,6W	125
PVC	DBSN	ETOH		50C/2,4,6W	125
PVC	DBSN	HC		50C/2,4,6W	125
PVC	DBSN	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	DBSN	HOAC		50C/2,4,6W	125
PVC	DNP	AQ		ENI, 38-56C/TO 12D	86
PVC	DNP	AQ		NKD, 20-56C/TO 15D	182
PVC	DNP	AQ		ENI, 40-80C/TO 20D	183

PVC	DNP	DP		ENI, 38-56C/TO 12D	86
PVC	DNP	DP		NKD, 20-56C/TO 15D	182
PVC	DNP	DP		20-60C/TO 20D, ENI	184
PVC	DNP	DP		40-70C/TO 12D, ENI	185
PVC	DNP	H2O		ENI, 38-56C/TO 12D	86
PVC	DNP	H2O		NKD, 20-56C/TO 15D	182
PVC	DNP	H2O		40-70C/TO 12D, ENI	185
PVC	DOP	AC		50C/2,4,6W	125
PVC	DOP	BL	GC	NS, 4C/5-21D	75
PVC	DOP	ETOH	RAD	25C/TO 50D	78
PVC	DOP	ETOH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DOP	ETOH	TLC	NKD, 1-5%DOP, 45C/2D	188
PVC	DOP	ETOH		50C/2,4,6W	125
PVC	DOP	ET2O	GC	NKD, TO 98C/TO 10D	10
PVC	DOP	ET2O	TLC	NKD, 1-5%DOP, 45C/2D	188
PVC	DOP	HC	GC	NKD, TO 98C/TO 10D	10
PVC	DOP	HC	RAD	20-60PHR, 10-60C/2-80D	79
PVC	DOP	HC	TLC	NKD, 1-5%DOP, 45C/2D	188
PVC	DOP	HC		50C/2,4,6W	125
PVC	DOP	H2O	GC	100C/6H	18
PVC	DOP	H2O	RAD	GR: 22-80C/5H-90D	12
PVC	DOP	H2O	TLC	NKD, 1-5%DOP, 45C/2D	188
PVC	DOP	HCAC		50C/2,4,6W	125
PVC	DOP	MEOH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DOP	OIL	GC	NKD, TO 98C/TO 10D	10
PVC	DOP	OIL	RAD	APP, NKD, 0.25-25%, 20C/60D, 40C/10D	40
PVC	DOP	OIL	RAD	APP, 0.25-25%DOP, GR: TO 40C/TO 30D	43
PVC	DOP	OIL	RAD	20-60PHR, 10-60C/1-70D	81
PVC	DOP	OIL	RAD	NKD,	92
PVC	DOP	OIL		APP, CMT, SECT, CP, FAT-MIGRATION, 40C/1,2,4,9,16,25D	130
PVC	DOP	RCH	RAD	20-60PHR, 10-60C/1-80D	80
PVC	DOP	TG	GC	NKD, TO 98C/TO 10D	10
PVC	DOP		RAD	20-60PHR, 10-60C/1-70D	81
PVC	DOP			INTER-POLYMER, APP, 70C/TO 1320D	112
PVC	DOSN	AQ		ENI, 38-56C/TO 12D	86
PVC	DOSN	AQ		ENI, 40-80C/TO 20D	183
PVC	DOSN	DP		ENI, 38-56C/TO 12D	86
PVC	DOSN	DP		20-60C/TO 20D, ENI	184
PVC	DOSN	DP		40-70C/TO 12D, ENI	185
PVC	DOSN	ETOH	RAD	NKD, 20C/8W	91
PVC	DOSN	ET2O	GC	NKD, TO 98C/TO 10D.	10
PVC	DOSN	ET2O	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PVC	DOSN	FHC	RAD	20C/43,60D	54
PVC	DOSN	HC	GC	NKD, TO 98C/TO 10D	10
PVC	DOSN	HC	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PVC	DOSN	HC	RAD	20C/43,60D	54
PVC	DOSN	HC	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PVC	DOSN	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	DOSN	H2O		ENI, 38-56C/TO 12D	86
PVC	DOSN	H2O		40-70C/TO 12D, ENI	185
PVC	DOSN	MEOH	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PVC	DOSN	OIL	GC	NKD, TO 98C/TO 10D	10
PVC	DOSN	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PVC	DOSN	OIL	RAD	APP, 0.25-25%DOP, GR: TO 40C/TO 30D	43
PVC	DOSN	OIL	RAD	20C/30,60D	45
PVC	DOSN	OIL	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PVC	DOSN	OIL	RAD	NKD, 4-25%DOP, 40C/10D, APP	48
PVC	DOSN	OIL	RAD	65C/2,5H, GR: TO 6H	51

PVC	DOSN	OIL	RAD	20C/30,60D, GR: TO 60D	52
PVC	DOSN	OIL	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PVC	DOSN	OIL	RAD	20C/43,60D	54
PVC	DOSN	OIL	RAD	GR: 20-40C/0,1-30D	55
PVC	DOSN	OIL	RAD	20C/60D, 65C/5H, GR: 0,5-5H	132
PVC	DOSN	OIL	RAD	20C/30D, 45C/10D, NKD	155
PVC	DOSN	OIL	RAD	NKD, 0,10,20,30,45C/10D, 75C/2D	156
PVC	DOSN	OIL		4,20-25C/1,2,3,6M, 45C/10D	187
PVC	DOSN	R20	RAD	4-25%DOP, APP, 20C/30,60D, 40C/10D, GR: TO 80C/TO 80D	46
PVC	DOSN	R20	RAD	20C/43,60D	54
PVC	DOSN	TG	GC	NKD, TO 98C/TO 10D	10
PVC	DOSN	TG	RAD	65,83C/2,5H	39
PVC	DOSN	TG	RAD	20C/30,60D	45
PVC	DOSN	TG	RAD	65C/2,5H, GR: TO 6H	51
PVC	DOSN	TG	RAD	20C/30,60D, GR: TO 60D	52
PVC	DOSN	TG	RAD	APP, FAT-PENETRATION, 20C/30,60D, 65C/2,5H	53
PVC	HMBP	ETOH	TLC	NKD, 45C/10D	170
PVC	HMBP	HC	TLC	NKD, 45C/10D	170
PVC	HMBP	H2O	TLC	NKD, 45C/10D	170
PVC	HMBP	HOAC	TLC	NKD, 45C/10D	170
PVC	HMBP	OIL	TLC	NKD, 45C/10D	170
PVC	MGST	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	MMBP		RAD	D, K, INTER-POLYMER	13
PVC	MSN	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	MSN	OIL	RAD	20C/30D, 40C/10D, 70C/0,5H, GR: TO 30D	42
PVC	MSN	OIL	RAD	40C/5-240H	44
PVC	PAP	AQ		ENI, 38-56C/TO 12D	86
PVC	PAP	AQ		NKD, 20-56C/TO 15D	182
PVC	PAP	AQ		ENI, 40-80C/TO 20D	183
PVC	PAP	OP		ENI, 38-56C/TO 12D	86
PVC	PAP	OP		NKD, 20-56C/TO 15D	182
PVC	PAP	OP		20-60C/TO 20D, ENI	184
PVC	PAP	OP		40-70C/TO 12D, ENI	185
PVC	PAP	H2O		ENI, 38-56C/TO 12D	86
PVC	PAP	H2O		NKD, 20-56C/TO 15D	182
PVC	PAP	H2O		40-70C/TO 12D, ENI	185
PVC	PB			NC, 20-80C	165
PVC	RSE	AQ		ENI, 38-56C/TO 12D	86
PVC	RSE	AQ		ENI, 40-80C/TO 20D	183
PVC	RSE	OP		ENI, 38-56C/TO 12D	86
PVC	RSE	OP		20-60C/TO 20D, ENI	184
PVC	RSE	OP		40-70C/TO 12D, ENI	185
PVC	RSE	H2O		ENI, 38-56C/TO 12D	86
PVC	RSE	H2O		40-70C/TO 12D, ENI	185
PVC	SN	ETOH	COLOR	RT/1-138H, SURFACE-WASH	34
PVC	SN	ET2O		RT/0,5,1,11M	180
PVC	SN	HC		RT/0,5,1,11M	180
PVC	SN	H2O	COLOR	RT/1-138H, SURFACE-WASH	34
PVC	SN	HOAC		APP, NC, NS, NTT	1
PVC	SN	OIL		RT/0,5,1,11M	180
PVC	SN	VEG		APP, NC, NS, NTT	1
PVC	TEP	H2O	RAD	GR: 22-80C/5H-90D	12
PVC	TIO2	H2O	SPEC	5,50C/2,4,6,8W	30
PVC	TTB	ET2O	RAD	20C/60D, 65C/5H, GR: 0,5-5H	132
PVC	TTB	HC	RAD	20C/60D, 65C/5H, GR: 0,5-5H	132
PVC	TTB	MEOH	RAD	20C/60D, 65C/5H, GR: 0,5-5H	132
PVC	TTB	OIL	RAD	APP, 20C/60D, 65C/5H, GR: TO 65C/TO 60D	39
PVC	TTB	OIL	RAD	20C/30,60D	45

PVC	TTB	OIL	RAD	65C/2.5H, GR: TO 6H	51
PVC	TTB	OIL	RAD	20C/30.60D, GR: TO 60D	52
PVC	TTB	OIL	RAD	APP, FAT-PENETRATION, 20C/30.60D, 65C/2.5H	53
PVC	TTB	OIL	RAD	20C/60D, 65C/5H, GR: 0.5-5H	132
PVC	TTB	TG	RAD	65,83C/2,5H	38
PVC	TTB	TG	RAD	20C/30.60D	45
PVC	TTB	TG	RAD	65C/2.5H, GR: TO 6H	51
PVC	TTB	TG	RAD	20C/30.60D, GR: TO 60D	52
PVC	TTB	TG	RAD	APP, FAT-PENETRATION, 20C/30.60D, 65C/2.5H	53
PVC	VC	ETOH	GC	NS, 22C/3.6.9.12M, GR: TO 49C/TO 10Y	27
PVC	VC	ETOH	GM	SOL, SD, 30-90C	7
PVC	VC	ETOH		GR: 23-70C/0.01-720D	131
PVC	VC	HC	GC	NS, 22C/3.6.9.12M, GR: TO 49C/TO 10Y	27
PVC	VC	HC	GC	K, S/D	116
PVC	VC	H2O	GC	NS, 22C/3.6.9.12M, GR: TO 49C/TO 10Y	27
PVC	VC	H2O	GC	K, CMT, SD	62
PVC	VC	H2O	GC	K, SD, AC	63
PVC	VC	H2O	GC	K, S/D	116
PVC	VC	H2O	GM	SOL, SD, 30-90C	7
PVC	VC	H2O		MC, 23C/1-180D	5
PVC	VC	H2O		GR: 23-70C/0.01-720D	131
PVC	VC	HOAC	GC	NS, 22C/3.6.9.12M, GR: TO 49C/TO 10Y	27
PVC	VC	HOAC	GC	K, SD, AC	63
PVC	VC	HOAC		GR: 23-70C/0.01-720D	131
PVC	VC	OIL	GC	40C/10.20D, RT/35D, GR: TO 160D, CP	93
PVC	VC	OIL	GC	NS, 22C/3.6.9.12M, GR: TO 49C/TO 10Y	27
PVC	VC	OIL	GC	K, CMT, SD	62
PVC	VC	OIL	GC	K, S/D	116
PVC	VC	OIL		GR: 23-70C/0.01-720D	131
PVC	VC		GC	AIR, MODEL, GR: TO 38C/TO 30D	26
PVC	VC		GM	D, SD, CMT, 20-90C	9
PVC	ZNST	H2O	RAD	GR: 22-80C/5H-90D	12
PVC		MF	GC	4C/1.2.8.40	28
PVDC	DCP	OIL		APP, CMT, SECT, CP, FAT-MIGRATION, 40C/1.2.4.9.16.25D	130
PVDC		ETOH		GR: 23-70C/0.01-720D	131
PVDC		H2O		GR: 23-70C/0.01-720D	131
PVDC		HOAC		GR: 23-70C/0.01-720D	131
PVDC		OIL		GR: 23-70C/0.01-720D	131
SAN	AN	ETOH		GR: 23-70C/0.01-720D	131
SAN	AN	H2O		GR: 23-70C/0.01-720D	131
SAN	AN	HOAC		GR: 23-70C/0.01-720D	131
SAN	AN	OIL		GR: 23-70C/0.01-720D	131
SBR	BCO			D	141
SBR	HXD			D, CMT	139
SBR	MW		GM	BLOOM	158
SBR	WAX			TO 280D	19
V/APB	VAC	H2O		60C/1H, NKD	20
V/APB	VC	ETOH			14
V/APB	VC	H2O			14
PAN	AN	H2O	GC	K, SD, AC	63
PAN	AN	HOAC	GC	K, SD, AC	63
PVC/ABS	AN	ETOH	POLAR	NKD, RT/4D	95
PVC/ABS	AN	H2O	POLAR	NKD, RT/4D	95
PVC/ABS	AN	HOAC	POLAR	NKD, RT/4D	95
PVC/ABS	AN	OIL	POLAR	NKD, RT/4D	95
PVC/ABS	BST	ETOH	POLAR	NKD, RT/4D	95
PVC/ABS	BST	H2O	POLAR	NKD, RT/4D	95
PVC/ABS	BST	HOAC	POLAR	NKD, RT/4D	95

PVC/ABS	BST	OIL	POLAR	NKD, RT/4D	95
PVC/ABS	DOP	ETCH	POLAR	NKD, RT/4D	95
PVC/ABS	DOP	H2O	POLAR	NKD, RT/4D	95
PVC/ABS	DOP	HOAC	POLAR	NKD, RT/4D	95
PVC/ABS	DOP	OIL	POLAR	NKD, RT/4D	95
PVC/ABS	S	ETCH	POLAR	NKD, RT/4D	95
PVC/ABS	S	H2O	POLAR	NKD, RT/4D	95
PVC/ABS	S	HOAC	POLAR	NKD, RT/4D	95
PVC/ABS	S	OIL	POLAR	NKD, RT/4D	95
PAT	XYZ	OIL	RAD	APP, 40C/10D	105
PES	XYZ	H2O		TC 50C/TO 8W	119
ABS/MA		ETCH		39-65C/1-7D, NKD	179
ABS/MA		H2O		39-65C/1-7D, NKD	179
ABS/MA		HOAC		39-65C/1-7D, NKD	179
ABS/MA				39-65C/1-7D, NKD	179
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REVIEW AND EVALUATION OF AVAILABLE MIGRATION MODELS

Introduction

Migration of minor constituents from a polymeric film to a food or simulating solvent is controlled by both transport and thermodynamic factors. Neither can be ignored if a complete description of migration is desired. For example, the diffusion of a species (hereafter referred to as the "migrant") from a polymer film of thickness 2ℓ and volume V_p to a stirred solvent of volume V_s is given by [1]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-Dq_n^2 t/\ell^2\right) \qquad (1)$$

where the q_n's are the non-zero positive roots of

$$\tan q_n + \alpha q_n = o \qquad (2)$$

and

$$\alpha = \left(V_s/V_p\right)K \qquad (3)$$

D= migrant diffusion constant in polymer

$K= C_s/C_p$ = equilibrium distribution coefficient

C_p= equilibrium concentration of migrant in film

C_s= equilibrium concentration of migrant in solvent

M_t= amount of migrant transfered to solvent at time t

M_∞= amount of migrant transfered to solvent at infinite time

If the initial concentration of migrant in the polymer film was C_o, then $M_o = V_p C_o$ and

$$1 - \frac{C_p}{C_o} = \frac{M_\infty}{M_o} = \frac{\alpha}{1+\alpha} \qquad (4)$$

Notice that Eq. (1) is a function of both D (a transport property) and K (a thermodynamic property). Equation (4) determins the maximum amount of migration that can occur and is strictly an equilibrium or thermodynamic property of the system.

Equation (1) is the complete solution for a certain class of migration problems; viz., those systems which obey Fick's two laws of diffusion and for which D and K are known. Therefore, modeling migration behavior for this type of system can be reduced to estimating, either theoretically or by semi-emperical methods, K and D.

If the polymer film is appreciably penetrated by solvent, the diffusion constant is not constant and Eq. (1) will no longer hold. But even in these systems Eq. (4), which is only a function of K, is valuable in the sense that it yields an upper limit for migration. Of course, this upper limit equals M_o (complete extraction of the migrant) if the solvent mass is much larger than the film mass; i.e., if the film is placed in an infinite solvent reservoir, migration continues to completion at infinite time. However, in many food packaging applications (e.g. plastic bottles) α will be finite and a residual amount of migrant will be retained by the film.

In the next section, methods of theoretically estimating distribution coefficients will be discussed which will then be followed by a discussion of theoretical methods for estimating diffusion constants. A general and practical migration model will ultimately depend on how well K and D (and their temperature dependences) can be calculated from the physical properties of the polymer, solvent, and migrant.

Distribution Coefficients

In principle, a relatively good estimate of K should be possible for some polymer/solvent/migrant systems by using either the Flory equation of state theory of solutions[2-4] or the lattice fluid (LF) theory of Sanchez and Lacombe[5]. An important prerequisite for the application

of either theory is that the thermodynamic behavior of the migrant + polymer can be treated as an equilibrium mixture of two fluids. The amorphous component of a semi-crystalline polymer, such as polyethylene, can be treated as an equilibrium liquid if the temperature is above the polymer glass transition temperature. Under these conditions, the chemical potential of any organic migrant species (liquid or gas) within the amorphous regions can be calculated.

According to the well-known Flory-Huggins (F-H) theory of solutions[6], the chemical potential of component 1 in a binary mixture is given by

$$(\mu_1 - \mu_1^o)/RT = \ln\phi_1 + (1 - V_1/V_2)\phi_2 + \chi\phi_2^2 \qquad (5)$$

where μ_1^o is the molar Gibbs free energy of pure liquid component 1 at temperature T, $\phi_1 = 1 - \phi_2$ is the volume fraction of component 1, V_1 and V_2 are the respective molar volumes of the two components and χ is the reduced residual chemical potential[4]. In the original formulation of F-H theory, χ was strictly an energetic parameter that was proportional to the energy required to form a 1-2 bond from a 1-1 and 2-2 bond. It also had a simple 1/T temperature dependence and was independent of solution composition. Now it is known that χ is in general concentration dependent and possesses a more complicated temperature dependence than 1/T. Experimentally, χ is treated as an empirical parameter which is adjusted as a function of concentration and temperature to fit experimentally determined chemical potentials.

Even in solutions containing polar components, positive χ values are usually required[4]. Large positive χ's are, of course, thermodynamically unfavorable and will limit miscibility.

This positive character of χ has highlighted the failure of F-H theory because the sign of χ should be the same as that of the heat of mixing, ΔH_m. Exothermic mixing requires a negative χ, yet there exist many examples where ΔH_m is negative and positive χ's are required for the chemical potentials. Even more puzzling within the context of F-H theory is that large negative heats of mixing often occur with mixtures of non-polar components which require relatively large positive χ values (see Table I for some examples). However, both the new Flory and LF theories have resolved this apparent paradox. Experimentally, χ often has a large positive entropic component which arises, according to the Flory and LF theories, from differences in the equation of state properties of the pure components.

Formally, the concentration dependence of χ can be expressed as

$$\chi = \chi_1 + \chi_2\phi_2 + \chi_3\phi_2^2 + \ldots \qquad (6)$$

There are two important limiting values of χ:

$$\chi_1 = \chi(\phi_1=1) \qquad (7)$$

$$\chi^\infty = \chi(\phi_1=0) = \sum_1^\infty \chi_i \qquad (8)$$

In almost all polymer solutions that have been studied, $\chi^\infty > \chi_1$ for the solvent chemical potential.

At equilibrium, the chemical potential (or activity) of the migrant μ_p in the amorphous regions of a semi-crystalline polymer will equal the chemical potential μ_s of the migrant in the solvent phase:

$$\mu_p = \mu_s \qquad (9)$$

Let the migrant be component 1 and present in small quantities compared to the polymer film or simulating solvent; thus $\phi_2 \rightarrow 1$ and the migrant chemical potentials approach the following limiting forms:

$$(\mu_p - \mu^o)/RT = \ln\phi_p + 1 + \chi_p^\infty \qquad (10)$$

$$(\mu_s - \mu^o)/RT = \ln\phi_s + (1 - V_m/V_s) + \chi_s^\infty \qquad (11)$$

where V_m and V_s are the molar volumes of migrant and solvent respectively ($V_m/V_p \simeq o$ and is ignored), ϕ_s is the migrant volume fraction in the solvent phase, ϕ_p is the migrant volume fraction in the polymer phase and χ_p^∞ and χ_s^∞ are the χ^∞ values of the migrant in polymer and solvent phases, respectively. At equilibrium, Eq. (9) holds and thus the distribution coefficient is given by

$$K = \phi_s/\phi_p = \exp\left(V_m/V_s + \chi_p^\infty - \chi_s^\infty \right) \qquad (12)$$

Equation (12) offers an alternative to extraction experiments for experimentally determining distribution coefficients. Recent advances in gas chromatographic techniques have made it possible to determine χ^∞ in low molecular weight systems such as n-hexane/squalene[7] and in polymer/solvent systems such as polyethylene/n-decane[8]. The necessary equations required to obtain chemical potentials from equilibrium chromatograms are discussed in references 7 and 8

and in more recent papers by Purnell[9] and Bonner and Brookmeier[10]. For polymers, measurements are normally carried out above the polymer melting point or glass transition temperature. These temperatures will usually be well above the anticipated use temperatures of the polymeric food packaging material. However, with the aid of theory, experimental χ^{∞} values can be extrapolated accurately to lower temperatures.

The Flory[2-4] and lattice fluid[5] (LF) theories incorporate the "equation of state" properties of the pure component fluids. Both theories require 3 equation of state parameters for each pure component which are determined from PVT data. For the LF, about 60 low molecular weight fluids[5] and 10 different polymers[11] have already been so characterized. For a binary mixture, LF theory requires 7 parameters: 3 for each pure component, which are already known or are calculable from PVT data, and a seventh parameter that characterizes the interaction between the two components. The Flory theory requires an eighth parameter that is related to the surface/volume properties of the pure components. A relatively concise review and comparison of these two theories has been given by Sanchez[12].

For the LF, χ^{∞} for component 1, the migrant, is given by

$$\chi^{\infty} = \frac{M_1}{v_1^* \rho_1^*} \left[\tilde{\rho}_2 X_1 + (\tilde{\rho}_1 - \tilde{\rho}_2)/\tilde{T}_1 + (\tilde{v}_2 - 1)\ln(1-\tilde{\rho}_2) - (\tilde{v}_1 - 1)\ln(1-\tilde{\rho}_1) + \ln(\tilde{\rho}_2/\tilde{\rho}_1) \right] \qquad (13)$$

where

M_1 = molecular weight of component 1 (migrant)

T_1^*, v_1^*, ρ_1^* = characteristic temperature, volume, and mass density, respectively, of the migrant

$\tilde{\rho}_1 = \rho_1/\rho_1^* = 1/\tilde{v}_1$ reduced migrant density

$\tilde{\rho}_2 = \rho_2/\rho_2^* = 1/\tilde{v}_2$ reduced polymer density or reduced simulating solvent density

$\tilde{T}_1 = T/T_1^*$ reduced migrant temperature

$$X_1 = \Delta P^* v_1^*/RT \tag{14}$$

and ΔP^* represents the net change in cohesive energy density upon mixing components 1 and 2 at the absolute zero of temperature. X_1 <u>is the only unknown parameter in Eq. (13)</u>. All others are known or derivable from pure component PVT data. An experimental value of χ^∞ would establish the value of X_1, of course, but other kinds of solution data (often more accessible experimentally) such as heats of mixing, critical temperatures, solution densities, etc. can be used to determine X_1. Thus, LF theory offers a method of calculating χ^∞ values without actually measuring chemical potentials directly. To illustrate this possibility, χ^∞ values have been calculated for some polyisobutylene solutions using ΔH_m data to fix X_1. As a polymer solution becomes dilute in polymer (component 2), the heat of mixing approaches a limiting value, $\Delta H_m(\infty)$, defined by:

$$\Delta H_m(\infty) = \lim_{\phi_2 \to 0} \Delta H_m/\phi_2 \tag{15}$$

In Table I $\Delta H_m(\infty)$ values at 298 K for polyisobutylene in n-pentane, n-octane, cyclohexane, and benzene are tabulated. A striking feature of the data is that 3 out of 4 of these non-polar solutions are exothermic. Notice, however, that all

of the calculated ΔP^* and X_1 values are positive as one might expect for these non-polar components. The calculated X_1 values have then been used in Eq. (13) to calculate χ^∞; the experimental χ^∞ values are also tabulated in Table I for comparison. Also listed are the experimental and theoretical values of $\chi_1 \equiv \chi\ (\phi=1)$ which shows how χ can vary with concentration. Although the agreement is not spectacular, it is encouraging. Similar results can be obtained with the Flory theory whereas the Flory-Huggins theory would fail miserably.

TABLE I

	$\Delta H_m(\infty)$ (J/mol)	$X_1 x 10^2$	Δp^* (MJ/m^3)	X^∞ expt.	X^∞ calc.	X_1 expt.	X_1 calc.	data references
n-pentane	-201	4.980	10.4	0.93	0.69	0.49	0.76	13, 14
n-octane	-159	2.128	6.04	0.5	0.38	0.46	0.43	13, 15
cyclohexane	- 38	2.442	4.91	0.50	0.36	0.47	0.34	13, 16
benzene	+1090	8.180	20.07	1.15	0.73	0.50	0.63	13, 17

Table I A comparison of experimental and theoretical reduced residual chemical potentials for polyisobutylene solutions at 298K.

Diffusion Constants

1. General Properties

Typically, the self-diffusion constant D of an organic liquid is about 10^{-9} m^2/sec. At low concentrations in a polymer, the same organic species diffuses at a drastically reduced rate; D can vary from about 10^{-13} m^2/sec at T_g + 100 K to about 10^{-20} m^2/sec near T_g.

Most diffusion studies have taken the form of permeation or sorption experiments performed on amorphous polymers (lightly crosslinked) above their glass transition temperatures. Whereas diffusion behavior is relatively simple at temperatures above T_g, it is exceedingly complex at temperatures near or below T_g.

In the usual absorption experiment a polymer film, initially free of diffusant molecules, is suddenly exposed to an organic vapor at a fixed pressure and the gain in weight of the film is monitored as a function of time. Desorption of the diffusant can also be studied by reducing the pressure to a new fixed value and following the film weight loss. Data from a sorption experiment (either absorption or desorption) are generally represented by plotting the amount of vapor M_t absorbed or desorbed against the square root of time. At long times equilibrium is approached and $M_t \rightarrow M_\infty$.

Crank[1] discusses at length the method of data analysis required to obtain diffusion constants from sorption data. It is assumed that D(c) is a function of concentration c, but not of time, and that the diffusant concentrations at

the film surface increase or decrease instantaneously with pressure to their equilibrium values. Under these conditions the sorption is called Fickian and sorption curves are expected to possess the following properties:

a) Sorption curves are initially linear in $t^{1/2}$. For absorption, the linear region extends to over 60% of M_∞. For desorption, linearity is obtained almost up to equilibrium if, as would normally be expected, $dD/dc > 0$.

b) Above the linear portions, both absorption and desorption are concave to the $t^{1/2}$ axis, irrespective of the form of D(c).

c) Sorption curves are superimposable. A series of absorption curves for films of different thicknesses (ℓ) are superposable if M_t is plotted against $t^{1/2}/\ell$. The same applies to a corresponding series of desorption curves.

These properties are independent of the form of D(c) and provide an experimental means of determining whether a given system exhibits Fickian sorption. <u>One of the most important findings of sorption studies is that at temperatures well above T_g, the sorption kinetics of organic vapors are invariably Fickian.</u>

Temperature dependent sorption studies have also revealed another characteristic property of small molecule diffusion in polymers: the temperature dependence is strong and non-Arrhenius. A plot of log D vs 1/T will usually be non-linear. For example, Hayes and Park[18] studied sorption of benzene in natural rubber and found that the apparent activation energy, $\Delta E^* \equiv -R\, d\ln D/d(1/T)$, is about 29kJ/mole at 373 K but increases to 96kJ/mol at 273 K.

Another feature of the temperature dependence, which is especially relevant for migration studies, is the finding that ΔE^* often appears to be independent of the diffusant's chain length or branching. Such has been the case for isomeric hydrocarbons in natural rubber[19] and polyisobutylene[20] and n-alkyl acetates in polymethyl acrylate[21,22]. In the case of natural rubber, the constancy of ΔE^* has been shown to hold up to as large a molecule as octadecane[23]. These findings tend to support the thesis that the temperature dependence of diffusion is largely determined by the properties of the polymer and is relatively independent of the size and shape of the diffusant.

2. Diffusion above T_g

Theories of the diffusion constant fall into two broad classes: In one, which is especially relevant for migration studies, attention is directed at how the magnitude of D and its temperature dependence are affected by such factors as the size and shape of the diffusant, the nature of the polymer, and the intermolecular interaction between diffusant and polymer. In the second class, interest is focused on interpreting the concentration and temperature dependence of D and not its magnitude. A 1973 review of the latter class of theories is available[24] while the former and more important class was reviewed in 1968 by Kumins and Kwei[25].

Of the theories reviewed in 1968, two stand out. These are the free volume theories of Cohen and Turnbull[26,27] and Bueche[28]. Both theories require the probability $P(v^*)$ that the local volume v associated with the molecule or a "segment" of the molecule be greater than some critical volume v^*. The theories are different in that different

methods are used for calculating $P(v^*)$. Cohen and Turnbull assumed that a multinomial distribution of free volumes exist in a liquid to derive:

$$P(v^*) = \exp(\gamma v^*/v_o f) \quad (16)$$

$$D \sim \bar{u}\, P(v^*) \quad (17)$$

where f is the fractional free volume, v_o is the molecular or segment volume when f=o, γ is a dimensionless constant ($1/2 < \gamma < 1$), and $\bar{u}$ is the average molecular or segment velocity [$\bar{u}=(kT/M)^{1/2}$]. Beuche used the thermodynamic theory of fluctuations, orginally derived by Einstein, to obtain

$$P(v^*) = \frac{1}{2}\,\mathrm{erfc}\left[\frac{v^* - \langle v\rangle}{(2\beta\langle v\rangle kT)^{1/2}}\right] \quad (17)$$

$$D \sim P(v^*) \quad (18)$$

where $\langle v\rangle$ is the average segment volume, β is the isothermal compressibility of the polymer and erfc is the complementary error function.

Although both of these theories in their original formulations did not consider the diffusion a small molecule in a polymer, they have been successfully applied to such systems. Fujita[29] has demonstrated that the Cohen-Turnbull theory adequately describes the temperature dependence of diffusion in polymers in several systems. (Acutally Fujita used an empirical equation for D due to Doolittle[30] which is equivalent to the Cohen-Turnbull equation for D). Fujita[29] and others[31-33] have shown that the Cohen-Turnbull theory, properly modified, adequately accounts for the concentration dependence of D up to 10% of diffusant. Kumins and Roteman[34] have used Bueche's theory successfully to correlate the diffusion behavior of small gas molecules with their van der Waal volumes.

However, the success of both theories must be viewed as being primarily correlative rather than truly predictive.

Recently Sanchez[35] obtained the following expression for the diffusion of a small molecule in a polymer:

$$D_o \equiv D(c=o) = \frac{\bar{u}}{6}\,(v^*)^{1/3}\,\mathrm{erfc}\left[\frac{v^* - \bar{v}^\infty}{(2\beta\bar{v}^\infty kT)^{1/2}}\right] \qquad (19)$$

where $\bar{v}^\infty$ is the <u>partial</u> <u>molar</u> <u>volume</u> of the diffusant in the limit of zero concentration, β is the compressibility of the polymer, and all other symbols have the same meaning as before. Equation (19) can also be suitably modified to treat the diffusion of a large molecule composed of N segments, each of which is able to execute independent diffusive motions.

Although Eq. (19) has yet to be tested quantitatively, it has the potential of being a predictive theory of diffusion. It is predictive in the sense that all of the requisite parameters and variables can be determined independently from other physical data; v^* can be determined from viscosity or self-diffusion data on the pure liquid diffusant; $\bar{v}^\infty$ can be semi-quantitatively calculated using either the Flory[2-4] or lattice fluid[5] theory of solutions; and β can be determined either experimentally or theoretically.

The attractive property of Eq. (19) is that it embodies all of the physical factors judged important for diffusion in polymers through v^*, $\bar{v}^\infty$, and β; v^* is a unique property of the shape and size of the diffusant; $\bar{v}^\infty$ is a property which depends sensitively on the polymer-diffusant intermolecular

interaction; and β, of course, is a characteristic property of the polymer.

Qualitatively, Eq. (19) also explains why the diffusion of a small molecule decreases by 4 or 5 orders of magnitude in a polymer. This can best be illustrated by expanding erfc X in an asymptotic series[36] so that Eq. (19) becomes (valid for large X):

$$D_o \approx \frac{\bar{u}}{6} \frac{(2\beta\bar{v}^{\infty} kT/\pi)^{1/2}}{v^* - \bar{v}^{\infty}} (v^*)^{1/3} \exp\left[- \frac{(v^*-\bar{v}^{\infty})^2}{2\beta\bar{v}^{\infty} kT} \right] \qquad (20)$$

The equation for the self-diffusion constant D_d of the diffusant will be the same as Eq. (19) or (20) except that $\bar{v}^{\infty}$ is replaced by the molar volume v_d of the diffusant and β is replaced by the compressibility β_d of the diffusant. Compressibilities of polymer liquids are just about one order of magnitude smaller than those of similar low molecular weight liquids. Thus, the big difference between D_d and D_o is the compressibility of the medium in which the diffusant molecule finds itself. (Volume fluctuations are directly proportional to β). Decreasing β by an order of magnitude can diminish D by a substantially larger amount since β appears in the exponential.

3. Diffusion below T_g

Analysis of migration or diffusion in polymers is often based on ideal conditions. That is, the diffusion constant is assumed to be constant independent of the concentration of the diffusing material in the polymer and the concentration in the polymer is assumed to be given by Henry's Law

$$C=kp \qquad (21)$$

at equilibrium, where p is the pressure of the diffusant in the gas surrounding the polymer or the concentration of the diffusant in a solution surrounding the polymer. However for some polymeric systems, especially glassy polymers, these conditions do not hold, so that a more complicated analysis is required.

Vieth[37] and others have studied diffusion and sorption in systems in which Eq. 21 is not obeyed. An example of such a system is methane in orientated polystyrene. The slope of the solubility versus pressure is not constant as in Eq. 21, but decreases with pressure and becomes constant at high pressures. Vieth and coworkers postulated that two modes of sorption are operative in such systems. The first mode of sorption, C_D, is proportional to the pressure, while the second mode of sorption, C_H, obeys Langmir sorption. Thus at equilibrium,

$$C = C_D + C_H = k_D p = \frac{C'_H bp}{1 + bp} \qquad (22)$$

The second mode of sorption, C_H, is considered to be due to holes or voids in the polymer. Methods have been given[37] to determine the constants k_D, b and $C_H{}^1$ in Eq. 22 from sorption curves. It was demonstrated that the equilibrium gas solubilities in glassy polymers may be characterized by the dual sorption model mathematically expressed by Eq. 22.

Vieth and Sladek[38] developed a theory of diffusion in systems that have dual sorption. They assumed the concentration in the Langmuir isotherm, C_H, of the adsorption did not contribute to diffusion and that the diffusion constant D of C_D, the Henry's law isotherm , is independent of concentration. They obtained the diffusion equation

$$D \frac{\partial^2 C_D}{\partial X^2} = \frac{\partial C_D}{\partial t} \left[1 + \frac{C'_H \, b/k_D}{(1+bC_D/k_d)^2} \right] \qquad (23)$$

and applied Eq.23 to transient sorption of CO_2 in Mylar. Eq. 23 could not be analytically solved for the boundary conditions of transient sorption because it is not linear in C_D. Therefore, numerical solutions of Eq. 23 were obtained for assumed values of b, C_H' and k_p. A method was given for matching these theoretical curves to the experimental sorption curves to obtain the diffusion constant D. Good agreement with the observed absorption was obtained. The method has since been applied to other systems exhibiting dual sorption.

Paul and Kemp[39] have investigated time lag experiments for systems exhibiting dual sorption. While Eq. 23 cannot be solved analytically for the boundary conditions (Barrer conditions) used for time lag experiments, analytic expressions for the permeability and time lags were derived. Kemp[40] made time lag experiments on a membrane of a silicone rubber impregnated with molecular sieve particles. Becasue the molecular sieve particles exhibited large Langmuir adsorption of the gases used, the membrane exhibited dual sorption.

He was able to determine the constants b, C_H', k_D and D from measurements of the silicone rubber and molecular sieves and predict the results of the time lag experiments. Good agreement was obtained.

The time lag experiment may be used to determine if a material obeys ideal diffusion. Fig. 1 shows the amount of CO_2 (AQ_t) diffused through a membrane versus the time. At times greater than 100 minutes, the amount increases linearly with time with a slope, transmission coefficient, of P = 0.1564 cc/min. Extrapolating this linear relationship (dashed curve) to $AQ_t = 0$ gives a time lag of 81 minutes. The amount of CO_2 versus time that would diffuse through the membrane for ideal diffusion with these values of the transmission coefficient and time lag has been computed and is shown by the crosses. This curve is far from the experimental curve indicating that diffusion of CO_2 in this membrane is not ideal. In fact, the membrane is one made by Kemp to have strong dual sorption. Thus, examination of the time lag curve of a membrane may be used to determine if the system shows ideal diffusion.

A simple test of ideal diffusion from a time lag experiment may be made as follows. Determine the transmission coefficient T and time lag θ for the system. Then for ideal diffusion, the amount of gas that has diffused through the membrane at a time equal to the time lag θ is given by $0.3343\theta T$.

If the amount of gas at the time lag differs from this value, the system does not exhibit ideal diffusion. For the case discussed, we obtain $0.3343 \times 81 \times 0.1564 = 3$ cc. Since the experiment gives 1 cc, the system does not obey ideal diffusion.

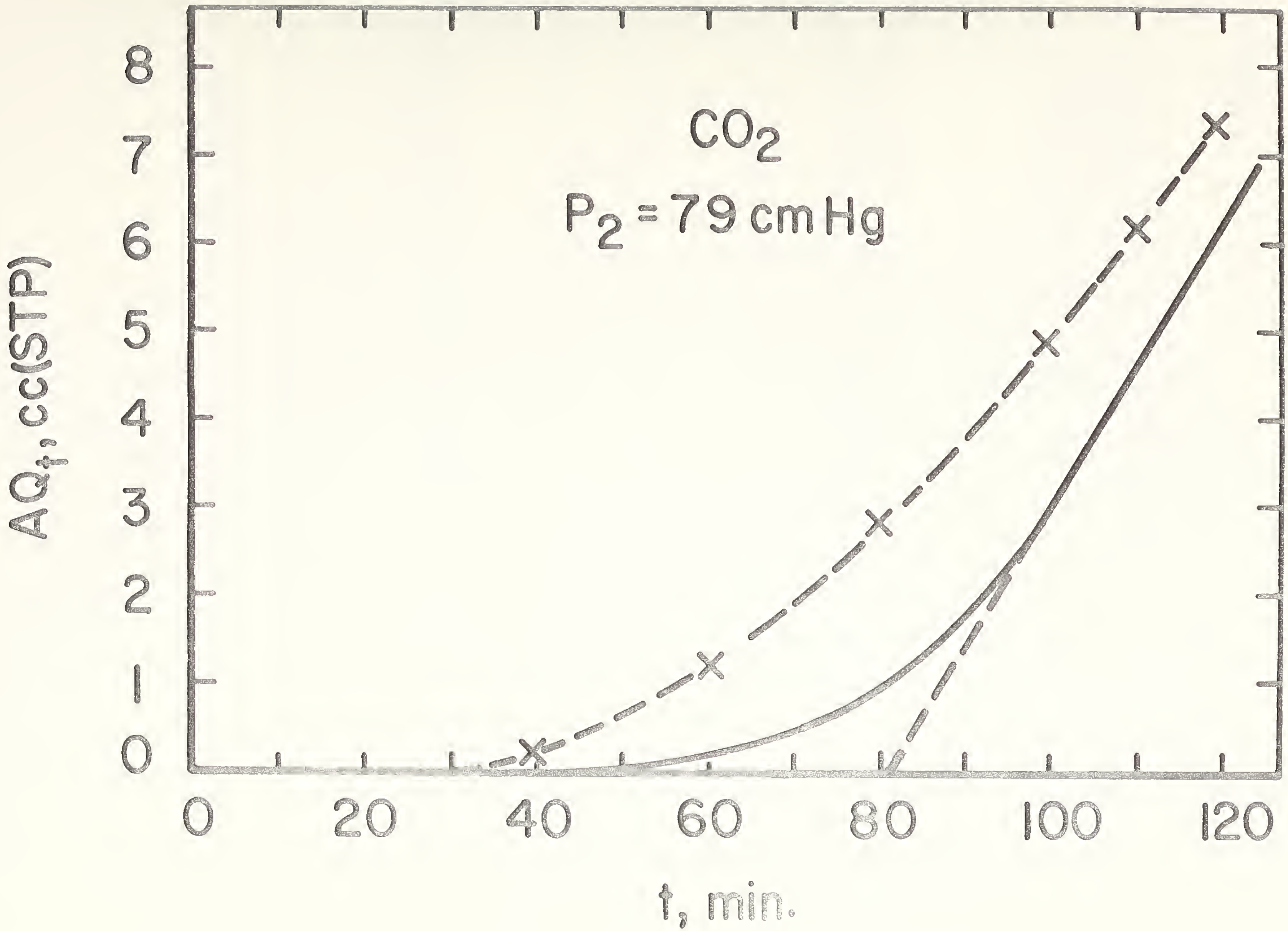

Figure 1. Amount of CO_2 diffused through a silicone rubber membrane impregnated with molecular sieve particles.

G. MISCELLANEOUS

N,N'-Diphenyl thiourea (thiocarbanilide)	0.5/PVC (c)
Cyanoguanidine (Dicyandiamide)	1/POM
N-n-Alkyl-N'-carboxymethyl-N,N'-trimethylenediglycine R = C_{14}-C_{18}	1.35/NR
p-*t*-Amylphenol-Formaldehyde Resins	2.1/PA
Nylon 66/610/6 terpolymer	1.5/POM
Poly(1,4-cyclohexylenedimethylene-3,3'-thiodipropionate) partially terminated with stearyl alcohol, MW1800-2200	0.5/PP/.005

D. PHENOLS (continued)

Tetra-:

Tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxy-bydrocinnamate)] methane Irganox 1010	.5/PO .05/E-MA, E-AA/.005 .5/PS,E-AA,E-VAc,S-B,IB 1/POM .5/POM

E. PHOSPHITES

Hydrogenated 4,4'-*i*-propylidene diphenol-phosphiteester resins 2400-3000	0.55/PVC (c)
4,4'-*i*-Propylidenediphenol alkyl (C_{12}-C_{15})-phosphites	1/PVC (c)
Tri(mixed mono- and dinonyl phenol) phosphite	
2-*t*-Butyl-*a*-(3-*t*-Butyl-4-hydroxyphenyl)-*p*-cumenyl bis(*p*-nonylphenyl)phosphite	1.35/NR,B-A,A-B-S,B-S/.004
Cyclic neopentanetetrayl bis(octadecyl phosphite)	0.25/PO 0.15/PO 0.20/PS,PS

F. THIO CARBOXYLIC ACIDS AND ESTERS

Thiodipropionic Acid

Dimyristyl thiodipropionate

Dicetyl thiodipropionate

Distearyl thiodipropionate
Antioxydans AS
Advastab PS 802

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PRELIMINARY CLASSIFICATION OF ADDITIVE TYPES

Introduction

A list of FDA approved additives (Section 178) for plastics to be used in contact with food are classified as to their chemical characteristics, along with their maximum allowable amounts (%)/ in particular types of plastics/and the maximum thickness of the plastics in inches.

Classification

A. ALCOHOLS AND ESTERS

1,3 - Butanediol	
Pantaerythritol	0.4/PVC
Pantearythritol stearate	0.4/PVC

B. BENZOPHENONES

2-Hydroxy-4-*n*-octoxy-benzophenone Advastab 46 Cyasorb UV531	0.5/PO
2-Hydroxy-4-*i*-octoxy-benzophenone Methanone [2-Hydroxy-4-(*i*-octoxy)phenyl]phenyl	0.5/PO(c)

C. METALLIC SALTS

1.	CALCIUM:	benzoate	
		myristate	
		ricinoleate	1/POM(c)
		stearate	
2.	COPPER:	cupric acetate	.025/NY66/.0012
		cupric carbonate	.005/NY66/.0015
		cuprous bromide	.0175/NY66/.0015
		cuprous iodide	.0025/NY66/.0015
3.	LITHIUM:	iodide	.065/NY66/.0012
4.	MAGNESIUM:	salicylate	0.3/RPVC(c)
5.	POTASSIUM:	bromide	0.18/NY66/.0015

6. TIN:	Di-*n*-octyl-tin maleate polymer	PVC
	Di-*n*-octyl-tin-bis(*i*-Octylmercapto-acetate)	PVC
	Poly[(1,3-di-butyl-di-Stann-thianediylidene)1,3-dithio]	0.2/PVC
7. ZINC:	dibutyldithiocarbamate	0.2/IB-IP(c)
	salicylate	0.3/RPVC
	palmitate	
	stearate	

D. PHENOLS

Mono-:

2,6-Di-*t*-butyl-*p*-cresol Ionol BHT Advastab 401	
2,6-Di-*t*-butyl-4-ethyl-phenol Antioxidant 724	0.1/E-P(c)/.0025 .025
2,6-Bis(1-methylheptadecyl)-*p*-cresol	.3/PO/.004
4-Hydroxy methyl-2, 6-di-t-butyl phenol Antioxidant 754	
n-Octadecyl-β-(4'-hydroxy-3'5'-di-*t*-butyl phenyl) propionate	.25/PO/.0025 .05/PO/no limit
Octadecyl-3,5-di-*t*-butyl-4-hydroxy-hydrocinnamate Irganox 1076	.25/PS,PS .5/A-B-S
2(2'-Hydroxy-5'-methyl phenyl)benzotriazole Tinuvin P	.25/PVC(c),PS
2(3'-*t*-Butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole Tinuvin 326	.5/PO
Butyrated styrenated cresols	.5/PS,PO

D. PHENOLS (continued)

Di-:

4,4'-Methylene-bis(2,6-di-*t*-butylphenol) Antioxidant 702	.25/PHC resins, turpene resins .5/PE,PB
2,2'-Methylene-bis(6-*t*-butyl-4-ethylphenol)	.6/A-B-S .1PA
2,2'-Methylene-bis(4-methyl-6-*t*-butylphenol)	.1/PO 1/POM(c) .5/POM
4,4'-Butylidene-bis(4-*t*-butyl-*m*-cresol)	.5/PP .3/PE
4,4'-Thio-bis(6-*t*-butyl-*m*-cresol) Santonox Advastab 415 Antioxydans KS	.25/PE
2,2'-Methylene-bis[6-(1-methylcyclohexyl)-*p*-cresol]	.2/PE/.0005
4,4'-Cyclohexylidene-bis(2-cyclohexylphenol)	.1/PO
2,2'-Methylene-bis(4-methyl-6-nonylphenol)	A-B-S

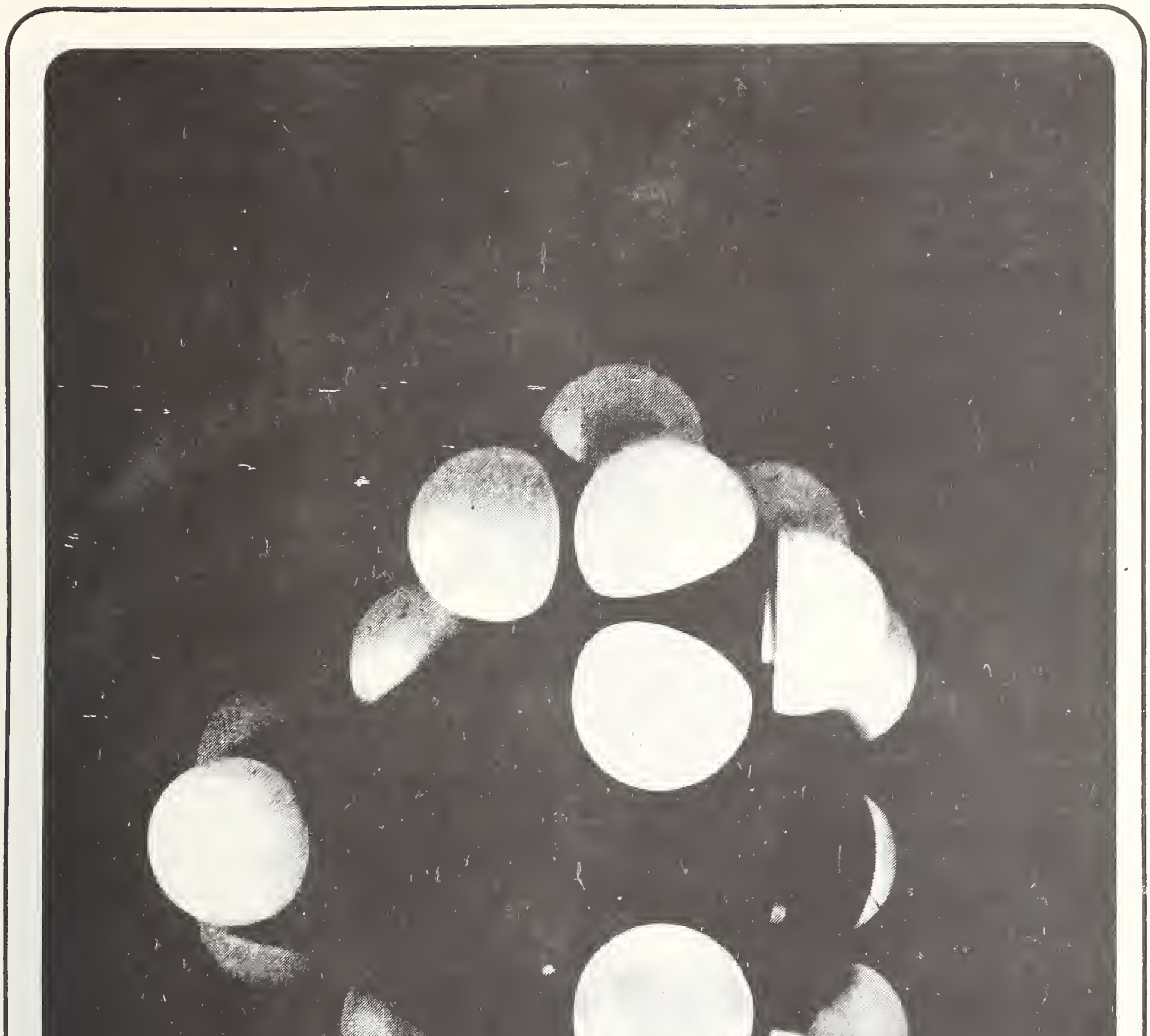
Tri-:

2,6-Bis(2-hydroxy-3-nonyl-5-methyl-benzyl)-*p*-cresol	A-B-S
Tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane	.25/A-B-S .1/A-B-S .2/PS
1,3,5-Trimethyl-2,4,6-tris- (3,5-di-*t*-butyl-4-hydroxybenzyl)benzene Ionox 330, Antioxidant 330	.5 1/NY
1,3,5-Tris (3,5-di-*t*-butyl-4-hydroxy-hydro- cinnamoyl)hexahydro-*s*-triazine	.25/PP .1/PE .5/E-P-EN/ .005/.005
1,3,5-Tris(3,5-di-*t*-butyl-4-hydrobenzyl)- 5-triazine-2,4,6(1H,3H,5H)trione	.25/PP .1/PE .5/PE .5/E-P-EN/ .005

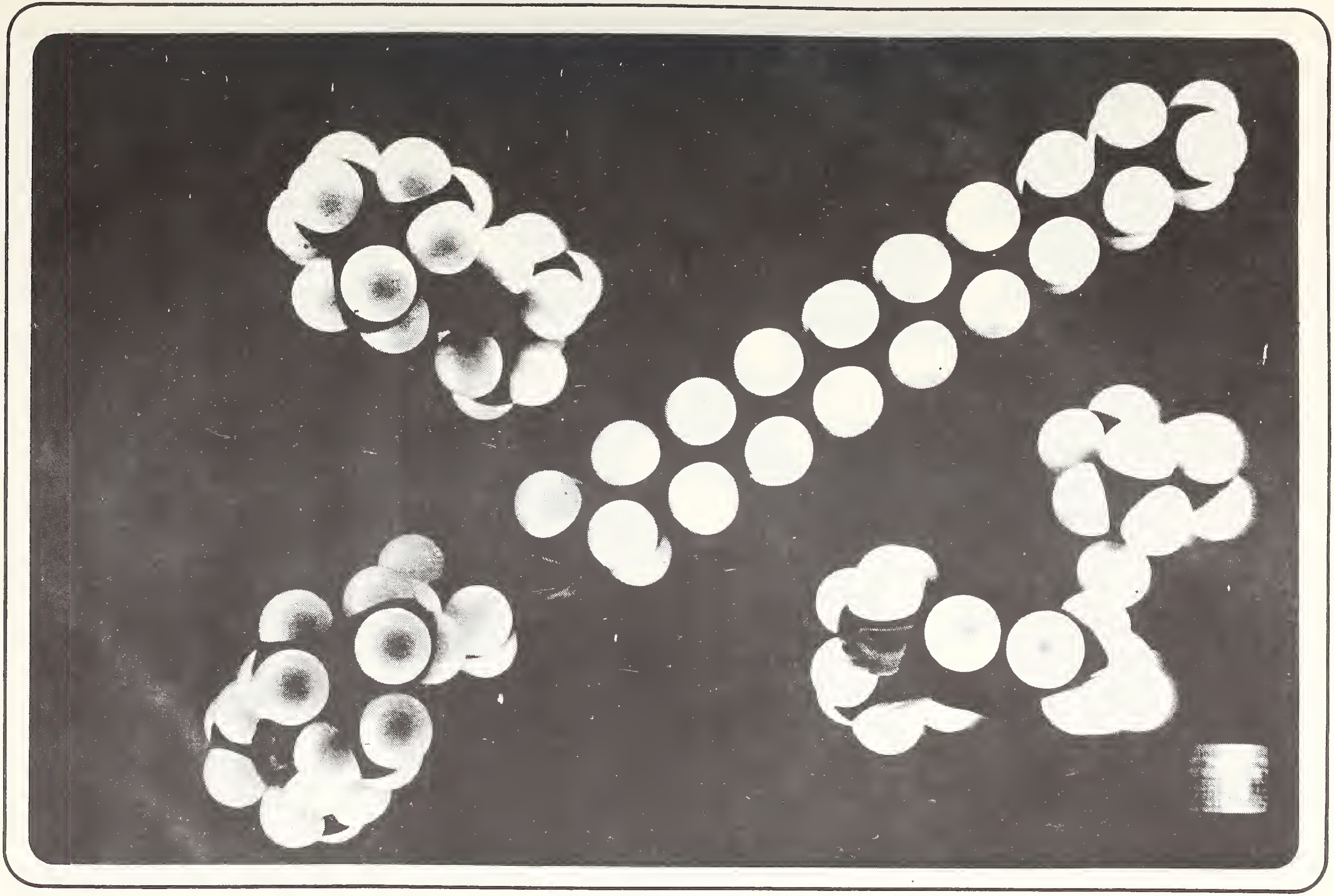
ABBREVIATIONS FOR POLYMERS

AA	Acrylic Acid
A	Acrylonitrile
B	Butadiene
(C)	Copolymer
E	Ethylene
EN	5-Ethylidine-2-norbornene
IB	Isobutylene
IP	Isoprene
MA	Methacrylic Acid
NR	Natural rubber
NY	Nylon
P	Propylene
PA	Polyamide
PBD	Polybutadiene
PE	Polyethylene
PHC	Petroleum hydrocarbon
PO	Polyolefin
POM	Polyoxymethylene
PP	Polypropylene
PVC	Poly(vinyl chloride)
S	Styrene
VAc	Vinyl acetate

Molecular Models of Some of the Additives
(0.1nm or 1Å is represented by 1.2 cm of the model)



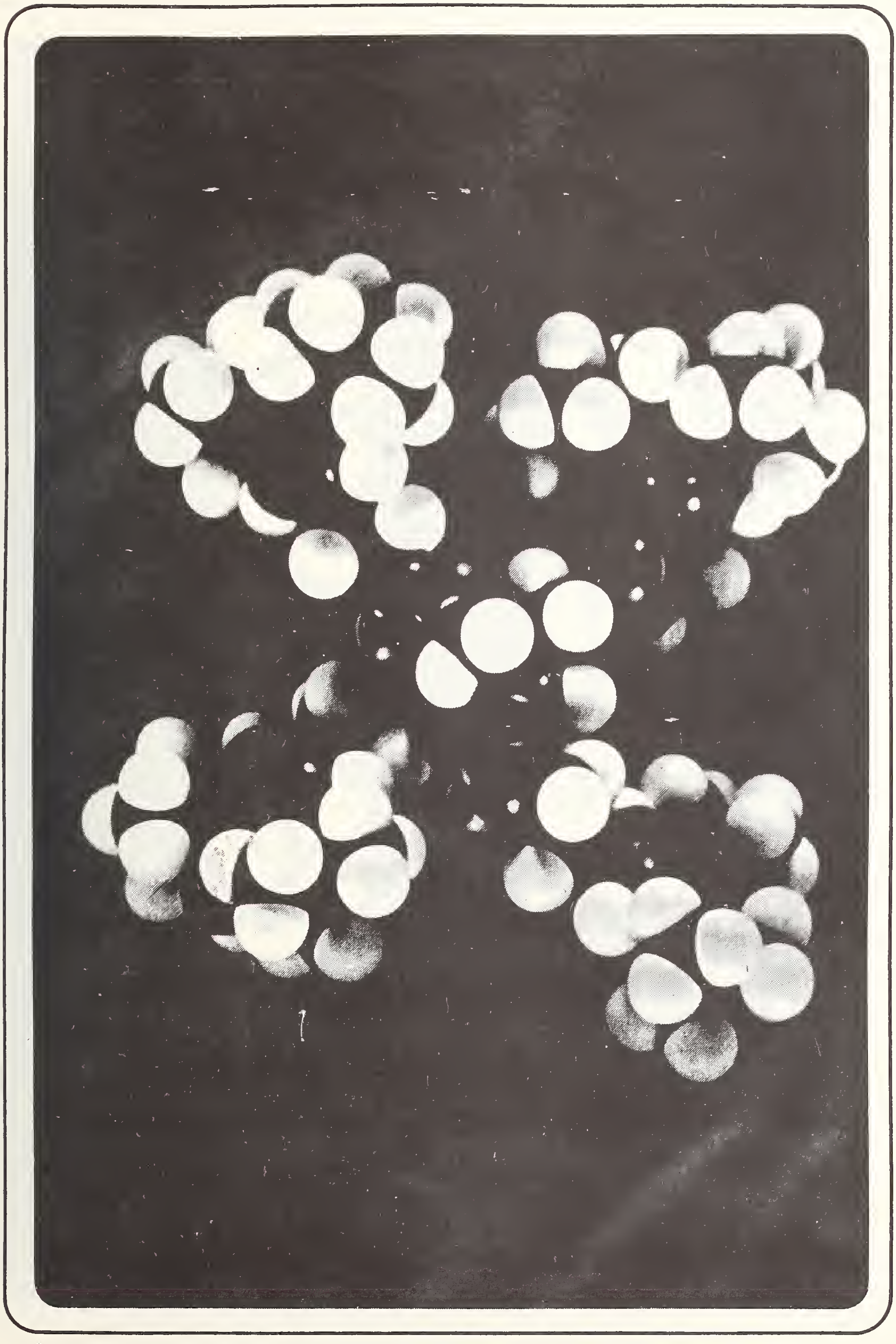
2,6-Di-*t*-butyl-*p*-cresol



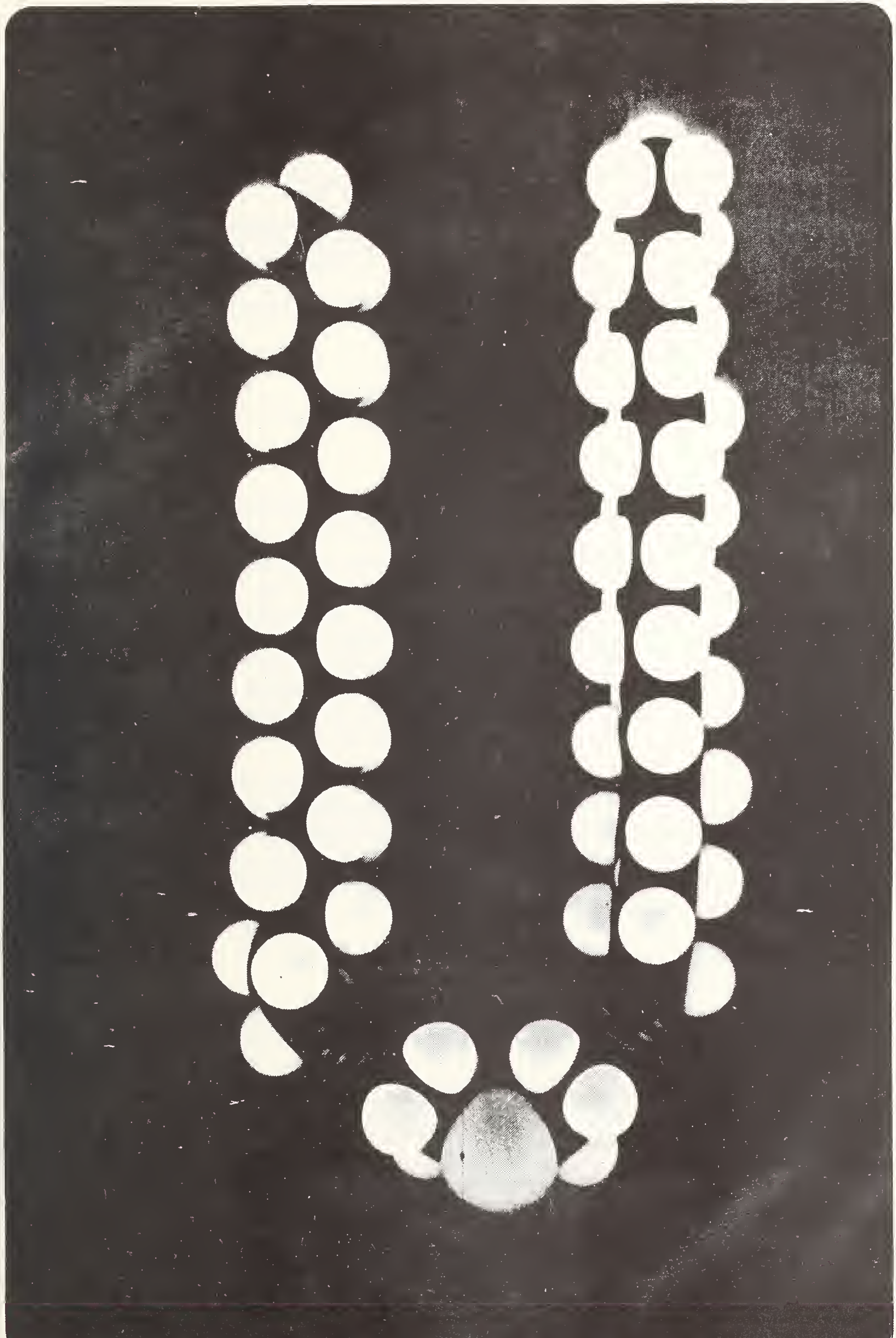
2,6-Di-*t*-butyl-*p*-cresol

n-Octadecyl 3,5-di-*t*-butyl-4-hydroxyhydrocinnamate

4,4'-Thio-bis(6-*t*-butyl-*m*-cresol)



Tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane



Distearyl thiopropionate

NBS-114A (REV. 7-73)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The objective of this work is the development of mathematical models that describe the migration of a variety of small molecules in polymers that have applications in food contact uses. In the most general cases, these models will be able to predict the amount of additive migration given any particular time and temperature history. These models can serve as the technical basis for more efficient regulatory methods under existing frameworks or in the design and implementation of new indirect additive regulations or policy.

The first steps in the development and assessment of such models are given in this report. The first section presents a preliminary survey of migration data applicable to food contact situations that are available in the current literature. The second section surveys available models describing migration and evaluates their present and potential utility.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Additives; diffusion; food additives; indirect additives; migration; models; regulation

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